

Redetermination of the Structure of [IrO₂{Ph₂PCH₂CH₂PPh₂}₂][PF₆]

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Abstract: The crystal structure of [IrO₂(C₆H₅)₂PCH₂CH₂P(C₆H₅)₂]₂[PF₆] has been redetermined from single-crystal X-ray diffraction data. The crystals were monoclinic of space group *P*2₁/*n* with four molecules in the unit cell of *a* = 17.18 (1) Å [17.24 (3)], *b* = 16.46 (1) Å [16.35 (3)], *c* = 16.97 (1) Å [16.98 (3)], and β = 95.02 (5)° [96.64 (2)°] (parameters from the previous X-ray determination in square brackets). The *R* of 6.7% from 2177 observed reflections in the earlier refinement has been reduced to 4.4% from 4007 observed reflections in this work. The most striking variation in this redetermination compared with the earlier work is (i) an O–O bond length of 1.52 (1) Å (cf. 1.625 (23) Å) and (ii) chemically equivalent sets of Ir–P bonds have similar bond lengths and are 2.308 (3) and 2.342 (3) Å (cf. 2.283 (7) and 2.452 (9) Å) (equatorial) and 2.353 (3) and 2.366 (3) Å (cf. 2.336 (7) and 2.349 (7) Å) (axial). A study of crystal decomposition caused by either heating or prolonged irradiation shows that these large differences are caused by systematic changes in the reflection intensities brought about by the decomposition.

From results of X-ray determinations^{2,3} on rhodium and iridium dioxygen complexes, one of the inferences drawn was that increasing the donor strength of the ligands favors longer O–O bonds. One crucial structure in this series was [IrO₂(DPE)₂][PF₆] which in the original refinement³ had two unusual parameters: a long O–O bond length of 1.625 (23) Å and two chemically equivalent Ir–P bonds differing greatly in length, i.e., 2.283 (7) and 2.452 (9) Å. Our crystallographic investigation of the complexes [MO₂L₄]X (M = Rh, Ir, L = PMe₂Ph, X = BPh₄; M = Ir, L₂ = bis(diphenylphosphinomethane), X = PF₆, ClO₄)⁴ and [RhO₂(AsMe₂Ph)₄][ClO₄]^{4,5} together with others of iridium,⁶ cobalt,⁷ and platinum⁸ have, however, found the O–O bond to be in a range approximately between 1.41 and 1.52 Å, implying that the O–O bond length is essentially independent of the metal and ligand involved. These results also suggested that the two unusual parameters in the [IrO₂(DPE)₂][PF₆] determination were erroneous, and a redetermination of the structure was therefore undertaken.

Experimental Section

Crystal Data. [IrO₂{P(C₆H₅)₂CH₂CH₂P(C₆H₅)₂}₂][PF₆]: M = 1166.0; monoclinic; space group *P*2₁/*n*; *a* = 17.18, *b* = 16.46, *c* = 16.97 (±0.01) Å; β = 95.02 (±0.05)°; *V* = 4781.6 Å³; *Z* = 4; *d*_m = 1.61, *d*_c = 1.62 g cm⁻³; Mo Kα λ 0.7107 Å, μ(Mo Kα) = 31.93 cm⁻¹.

Collection of Intensity Data. The compound was prepared by the published method.⁹ Recrystallization from dichloromethane-ethanol yielded orange prisms, many of which were twinned or of poor quality for crystallographic purposes. Intensity data were collected from a crystal (No. 1) of dimensions 0.28 × 0.32 × 0.40 mm on a Philips PW 1100 four-circle diffractometer for θ between 3 and 20° with graphite-monochromated Mo Kα radiation. Each reflection was scanned over 1° for 50 sec, and the same time was taken to accumulate the background count. The (0,4,0), (1,1,5), and (10,2,10) reflections were chosen as standards and remeasured every hour. During the 78 hr of data collection, the values of these standard intensities steadily decreased by 3, 2, and 13% respectively. Background and Lorentz-polarization corrections were applied to the 4452 measured intensities of which 4007 were classed as observed (intensities more than 2σ above the background intensity). Initially, no corrections were made for absorption, extinction, or crystal decomposition. Subsequently, the data were corrected for absorption, and the refinement process was repeated.

Refinement. 1. Data Not Corrected for Absorption. All calculations were performed on an IBM 360/65 computer with the X-RAY system of crystallographic programs.¹⁰ The scattering fac-

tor tables used were those of Cromer and Mann¹¹ corrected for anomalous scattering. Atomic positional parameters were obtained from the final parameters of McGinney, Payne, and Ibers, as well as independent Patterson and Fourier syntheses. Refinements of these two different sets of starting values led to the same results. Three cycles of full-matrix refinement of all positional parameters were performed, while keeping the thermal parameters constant. The thermal parameters of one-half of the atoms in the molecule were then refined for three cycles, while keeping the other half, as well as the positional parameters, constant. The remaining thermal parameters were then refined in the same manner, and the whole process was repeated, until all parameters had converged.

The final positional parameters and anisotropic temperature factors for all nonhydrogen atoms yielded a conventional *R* = 0.044 for the 4007 observed intensities. The unobserved data were then included, and the structure was again refined to convergence, giving *R* = 0.047. The differences between these two sets of parameters were never more than 2σ and usually less than σ. The resulting positional and thermal parameters and their calculated standard deviations are given in Table I. Bond lengths and angles calculated from the parameters in Table I are listed in Tables II and III, respectively. The numbering system is illustrated in Figure 1.

The difference Fourier maps were calculated using the final coordinates of the atoms. In the first, the two oxygen atoms were omitted from the structure factor calculations. The final map was featureless except for the two peaks expected for the oxygen atoms (relative heights 20 units) and some areas of height 2 units in the vicinity of the PF₆ ion. In the second map, the contribution of the PF₆ group was omitted from the structure factor calculations, but those of the two oxygen atoms were included. The map was featureless except for the expected electron density due to the PF₆ group (peak height of phosphorus was 41 units, those of the fluorines ranged from 11 to 14). The coordinates for the O, P, and F atoms deduced from these difference maps were within 0.002 of those obtained from the least-squares refinement. It was thus evident that, while the positions deduced for the oxygen atoms were reasonably accurate, there was some disordering of the PF₆ group that had not been allowed for. A second orientation was then included (weight 0.3, original orientation weight 0.7) and the structure refined for a further four cycles. No significant shifts were obtained in the parameters of the atoms of the [IrO₂(DPE)₂]⁺ cation, as can be seen in Table IV.

2. Data Corrected for Absorption. Ten cycles of least-squares refinement were carried out but with weights 1/σ_F². This converged to *R* = 0.046 with the final parameters within 3σ of those obtained previously. A final difference map was featureless.

Crystal Decomposition. Because the observed unit cell dimensions differed significantly from those reported previously,³ they were remeasured for several crystals. It was soon evident that the β

Table 1. Final Least-Squares Parameters with Estimated Standard Deviations in Parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁ ^a	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ir	0.3096 (1)	0.2272 (1)	0.0922 (1)	0.0349 (3)	0.0339 (3)	0.0321 (3)	-0.0015 (2)	0.0032 (2)	-0.0007 (2)
P ₁	0.3277 (2)	0.3059 (2)	-0.0173 (2)	0.0437 (16)	0.0292 (15)	0.0386 (16)	0.0005 (13)	0.0033 (13)	0.0040 (12)
P ₂	0.1846 (1)	0.2042 (2)	0.0258 (2)	0.0347 (15)	0.0405 (17)	0.0427 (16)	0.0005 (13)	0.0000 (13)	-0.0033 (13)
P ₃	0.4287 (2)	0.2538 (2)	0.1671 (1)	0.0376 (15)	0.0412 (16)	0.0375 (15)	-0.0058 (13)	0.0021 (12)	-0.0015 (13)
P ₄	0.3750 (1)	0.1115 (2)	0.0522 (1)	0.0340 (15)	0.0372 (16)	0.0343 (15)	-0.0017 (12)	0.0030 (12)	0.0028 (12)
O ₁	0.2534 (4)	0.2902 (4)	0.1748 (4)	0.0508 (45)	0.0635 (52)	0.0487 (44)	0.0132 (38)	0.0217 (35)	-0.0206 (38)
O ₂	0.2559 (4)	0.1997 (5)	0.1928 (4)	0.0555 (47)	0.0673 (55)	0.0514 (46)	0.0005 (40)	0.0160 (37)	-0.0124 (40)
C ₁₁	0.2647 (6)	0.2624 (6)	-0.0997 (6)	0.0498 (68)	0.0545 (71)	0.0410 (63)	-0.0169 (56)	-0.0046 (52)	0.0054 (54)
C ₂₁	0.1808 (6)	0.2544 (7)	-0.0731 (6)	0.0517 (72)	0.0684 (81)	0.0474 (68)	-0.0039 (61)	-0.0068 (55)	0.0153 (60)
C ₃₁	0.5065 (6)	0.2041 (6)	0.1160 (6)	0.0345 (58)	0.0422 (64)	0.0643 (71)	-0.0053 (50)	0.0099 (51)	-0.0027 (54)
C ₄₁	0.4791 (5)	0.1167 (6)	0.0965 (6)	0.0278 (56)	0.0425 (65)	0.0649 (71)	-0.0003 (48)	-0.0079 (50)	-0.0069 (54)
P ₅	-0.2533 (2)	0.2137 (2)	0.1556 (2)	0.0520 (18)	0.0573 (19)	0.0573 (19)	-0.0033 (16)	0.0026 (15)	-0.0051 (16)
C ₁₂	0.4228 (6)	0.3219 (6)	-0.0543 (6)	0.0536 (69)	0.0334 (62)	0.0534 (70)	0.0042 (55)	0.0154 (57)	0.0121 (55)
C ₁₂₁	0.4742 (6)	0.3768 (7)	-0.0121 (6)	0.0592 (78)	0.0467 (72)	0.0542 (71)	-0.0051 (61)	0.0054 (60)	0.0119 (58)
C ₁₂₂	0.5512 (7)	0.3853 (7)	-0.0337 (7)	0.0627 (82)	0.0579 (79)	0.0620 (79)	-0.0130 (64)	0.0033 (64)	0.0209 (65)
C ₁₂₃	0.5756 (7)	0.3425 (7)	-0.0985 (8)	0.0711 (88)	0.0581 (83)	0.0831 (96)	0.0013 (71)	0.0150 (74)	0.0127 (74)
C ₁₂₄	0.5220 (7)	0.2919 (7)	-0.1425 (7)	0.0677 (87)	0.0507 (77)	0.0834 (92)	0.0115 (67)	0.0197 (72)	0.0151 (69)
C ₁₂₅	0.4439 (6)	0.2819 (6)	-0.1220 (6)	0.0588 (77)	0.0428 (68)	0.0580 (74)	0.0111 (57)	0.0189 (60)	0.0166 (59)
C ₁₃	0.2907 (6)	0.4101 (6)	-0.0141 (6)	0.0445 (64)	0.0356 (63)	0.0573 (74)	-0.0027 (51)	0.0024 (54)	0.0009 (58)
C ₁₃₁	0.2821 (7)	0.4545 (6)	-0.0839 (6)	0.0778 (83)	0.0361 (69)	0.0553 (75)	0.0108 (61)	0.0135 (61)	0.0181 (58)
C ₁₃₂	0.2535 (7)	0.5344 (7)	-0.0841 (7)	0.0716 (84)	0.0580 (86)	0.0707 (87)	0.0116 (68)	0.0207 (68)	0.0125 (68)
C ₁₃₃	0.2316 (7)	0.5686 (7)	-0.0148 (8)	0.0645 (82)	0.0494 (77)	0.0903 (100)	0.0106 (64)	0.0152 (72)	0.0108 (74)
C ₁₃₄	0.2414 (7)	0.5252 (7)	0.0552 (7)	0.0697 (83)	0.0572 (85)	0.0702 (86)	-0.0056 (67)	0.0184 (67)	-0.0120 (69)
C ₁₃₅	0.2690 (6)	0.4438 (6)	0.0563 (6)	0.0583 (72)	0.0343 (67)	0.0550 (73)	-0.0032 (55)	0.0096 (57)	-0.0074 (55)
C ₂₂	0.1525 (5)	0.0997 (6)	0.0123 (6)	0.0278 (56)	0.0427 (65)	0.0553 (71)	-0.0061 (49)	0.0111 (51)	-0.0168 (58)
C ₂₂₁	0.1643 (6)	0.0495 (6)	0.0795 (6)	0.0345 (60)	0.0483 (72)	0.0523 (70)	0.0035 (53)	0.0092 (51)	0.0035 (58)
C ₂₂₂	0.1391 (6)	-0.0320 (7)	0.0740 (7)	0.0467 (71)	0.0618 (85)	0.0732 (86)	-0.0034 (62)	0.0080 (62)	-0.0051 (67)
C ₂₂₃	0.1038 (7)	-0.0629 (7)	0.0020 (8)	0.0537 (79)	0.0624 (86)	0.1030 (110)	-0.0007 (67)	-0.0026 (75)	-0.0162 (82)
C ₂₂₄	0.0917 (8)	-0.0124 (8)	-0.0635 (7)	0.0823 (95)	0.0726 (97)	0.0643 (86)	-0.0162 (78)	-0.0054 (71)	-0.0122 (74)
C ₂₂₅	0.1155 (6)	0.0703 (7)	-0.0587 (7)	0.0534 (72)	0.0628 (84)	0.0602 (79)	-0.0141 (63)	0.0090 (60)	-0.0108 (64)
C ₂₃	0.1046 (6)	0.2508 (8)	0.0736 (6)	0.0317 (62)	0.0590 (80)	0.0555 (71)	-0.0008 (56)	-0.0073 (53)	-0.0085 (59)
C ₂₃₁	0.1024 (7)	0.3357 (8)	0.0797 (8)	0.0579 (82)	0.0607 (89)	0.0933 (99)	-0.0030 (68)	-0.0173 (71)	-0.0235 (75)
C ₂₃₂	0.0389 (7)	0.3732 (8)	0.1171 (8)	0.0606 (86)	0.0835 (101)	0.0944 (103)	0.0237 (78)	-0.0202 (76)	-0.0512 (85)
C ₂₃₃	-0.0190 (7)	0.3226 (10)	0.1428 (7)	0.0613 (88)	0.1240 (131)	0.0535 (80)	0.0170 (89)	-0.0085 (66)	-0.0374 (86)
C ₂₃₄	-0.0163 (7)	0.2394 (10)	0.1362 (8)	0.0616 (88)	0.1108 (122)	0.0829 (99)	0.0251 (87)	0.0139 (75)	-0.0146 (90)
C ₂₃₅	0.0462 (6)	0.2033 (8)	0.1010 (7)	0.0431 (71)	0.0932 (98)	0.0609 (77)	0.0136 (71)	0.0148 (61)	-0.0102 (71)
C ₃₂	0.4625 (6)	0.3571 (6)	0.1888 (5)	0.0670 (78)	0.0527 (72)	0.0258 (56)	-0.0303 (63)	0.0012 (51)	0.0031 (51)
C ₃₂₁	0.5422 (7)	0.3753 (7)	0.1877 (6)	0.0741 (87)	0.0609 (82)	0.0531 (72)	-0.0325 (68)	-0.0027 (61)	-0.0031 (61)
C ₃₂₂	0.5684 (8)	0.4549 (8)	0.2096 (7)	0.0951 (102)	0.0703 (95)	0.0629 (83)	-0.0310 (81)	0.0109 (73)	-0.0002 (71)
C ₃₂₃	0.5152 (9)	0.5129 (8)	0.2297 (7)	0.1181 (120)	0.0611 (88)	0.0517 (77)	-0.0296 (85)	-0.0010 (78)	0.0095 (66)
C ₃₂₄	0.4374 (9)	0.4948 (8)	0.2309 (7)	0.1161 (115)	0.0572 (88)	0.0569 (80)	-0.0030 (81)	0.0062 (77)	-0.0014 (66)
C ₃₂₅	0.4084 (7)	0.4150 (7)	0.2107 (6)	0.0865 (87)	0.0376 (69)	0.0489 (69)	0.0035 (65)	0.0030 (61)	-0.0062 (55)
C ₃₃	0.4354 (6)	0.2109 (7)	0.2670 (6)	0.0605 (74)	0.0531 (71)	0.0433 (66)	-0.0274 (61)	-0.0151 (58)	0.0043 (56)
C ₃₃₁	0.4955 (7)	0.1566 (7)	0.2932 (7)	0.0673 (79)	0.0537 (74)	0.0592 (78)	-0.0227 (64)	-0.0289 (62)	0.0105 (61)
C ₃₃₂	0.4976 (9)	0.1274 (9)	0.3728 (8)	0.0996 (111)	0.0859 (103)	0.0758 (100)	-0.0393 (88)	-0.0255 (82)	0.0222 (83)
C ₃₃₃	0.4421 (9)	0.1545 (10)	0.4216 (8)	0.0982 (112)	0.1163 (127)	0.0504 (83)	-0.0445 (99)	-0.0111 (76)	0.0202 (83)
C ₃₃₄	0.3836 (8)	0.2111 (9)	0.3956 (7)	0.0986 (108)	0.1083 (117)	0.0529 (86)	-0.0546 (93)	-0.0009 (74)	0.0128 (79)
C ₃₃₅	0.3784 (7)	0.2402 (8)	0.3168 (6)	0.0676 (80)	0.0889 (93)	0.0369 (68)	-0.0377 (71)	0.0078 (59)	-0.0025 (64)
C ₄₂	0.3475 (5)	0.0163 (6)	0.0989 (6)	0.0390 (60)	0.0381 (65)	0.0485 (68)	0.0021 (49)	0.0083 (49)	0.0127 (53)
C ₄₂₁	0.3437 (6)	-0.0578 (6)	0.0582 (7)	0.0501 (68)	0.0330 (66)	0.0716 (77)	0.0026 (53)	0.0066 (57)	0.0110 (61)
C ₄₂₂	0.3293 (7)	-0.1304 (7)	0.0994 (7)	0.0628 (77)	0.0480 (75)	0.0714 (84)	0.0021 (59)	0.0189 (63)	0.0091 (64)
C ₄₂₃	0.3191 (6)	-0.1269 (7)	0.1806 (7)	0.0508 (71)	0.0572 (80)	0.0816 (93)	0.0019 (61)	0.0076 (63)	0.0355 (71)
C ₄₂₄	0.3225 (7)	-0.0528 (7)	0.2192 (7)	0.0599 (75)	0.0728 (89)	0.0515 (72)	-0.0023 (66)	0.0097 (58)	0.0198 (68)
C ₄₂₅	0.3361 (6)	0.0199 (7)	0.1803 (6)	0.0473 (67)	0.0679 (82)	0.0468 (71)	0.0029 (58)	0.0062 (53)	0.0110 (61)
C ₄₃	0.3807 (6)	0.0851 (5)	-0.0516 (5)	0.0526 (67)	0.0241 (54)	0.0369 (57)	0.0092 (49)	0.0126 (52)	0.0105 (45)
C ₄₃₁	0.4510 (6)	0.0962 (6)	-0.0869 (6)	0.0578 (73)	0.0491 (69)	0.0528 (73)	0.0080 (56)	0.0203 (58)	0.0173 (57)
C ₄₃₂	0.4521 (7)	0.0750 (7)	-0.1669 (6)	0.0774 (85)	0.0504 (72)	0.0474 (74)	0.0123 (64)	0.0203 (62)	0.0112 (58)
C ₄₃₃	0.3868 (8)	0.0415 (7)	-0.2090 (6)	0.0934 (97)	0.0511 (74)	0.0447 (70)	0.0122 (69)	0.0150 (68)	0.0001 (58)
C ₄₃₄	0.3175 (7)	0.0298 (7)	-0.1744 (6)	0.0827 (88)	0.0517 (73)	0.0419 (71)	0.0007 (64)	0.0003 (62)	-0.0002 (57)
C ₄₃₅	0.3143 (6)	0.0509 (6)	-0.0952 (6)	0.0471 (65)	0.0428 (63)	0.0402 (65)	-0.0011 (52)	0.0001 (51)	-0.0002 (51)
F ₁	-0.1983 (5)	0.2326 (7)	0.0900 (5)	0.0933 (60)	0.2372 (119)	0.1179 (69)	0.0232 (69)	0.0406 (53)	0.0517 (75)
F ₂	-0.3128 (5)	0.2746 (6)	0.1095 (5)	0.0824 (55)	0.1446 (80)	0.1635 (81)	0.0229 (54)	0.0190 (53)	0.0632 (67)
F ₃	-0.2984 (8)	0.1472 (6)	0.1086 (6)	0.2934 (144)	0.1031 (72)	0.1138 (73)	-0.0614 (84)	-0.0228 (82)	-0.0304 (60)
F ₄	-0.1949 (6)	0.1565 (7)	0.1996 (6)	0.0982 (66)	0.1871 (105)	0.2478 (124)	0.0596 (70)	0.0230 (72)	0.1197 (98)
F ₅	-0.2108 (7)	0.2830 (7)	0.2030 (7)	0.2273 (116)	0.1493 (92)	0.1332 (81)	-0.1049 (87)	-0.0014 (77)	-0.0436 (71)
F ₆	-0.3099 (4)	0.1996 (7)	0.2203 (4)	0.0758 (52)	0.2570 (121)	0.0817 (54)	-0.0365 (65)	0.0130 (43)	0.0187 (66)

^a Form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(a^2h^2U_{11} + b^2k^2U_{22} + c^2l^2U_{33} + 2a*b*hkU_{12} + 2a*c*hlU_{13} + 2b*c*klU_{23})]$.

angle was very much affected by crystal damage.

A study was made of the variation of the angle β with time of irradiation and heating. These results are given in Tables V and VI below and illustrated in Figure 2. The effect of heating a crystal was also followed on a Reichert hot-stage microscope (setting 150°C) using Nicol prisms and polarized light to indicate phase changes. No change was observed below 100°C. At 110°C cracks

developed across the surface, spreading down into the body as the temperature rose. Between 120 and 130°C, the crystal darkened to deep red and finally became nearly black and opaque. The time taken to go from 100 to 130°C was about 30 min. The crystal did not melt or crumble.

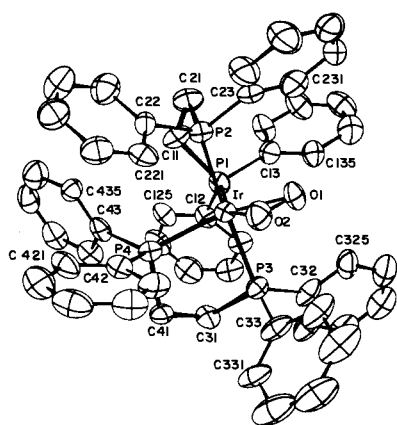
A systematic study was therefore made of the effect of decomposition on both the observed intensities and the derived heavy

Table II. Selected Intramolecular Bond Distances (Å)

Bond	Distance	Bond	Distance
Ir-P ₁	2.308 (3)	P ₄ -O ₁	4.26 (1)
Ir-P ₂	2.366 (3)	P ₄ -O ₂	3.58 (1)
Ir-P ₃	2.353 (3)	P ₁ -C ₁₁	1.84 (1)
Ir-P ₄	2.342 (3)	P ₂ -C ₂₁	1.87 (1)
Ir-O ₁	2.052 (7)	P ₃ -C ₃₁	1.85 (1)
Ir-O ₂	2.062 (7)	P ₄ -C ₄₁	1.88 (1)
P ₁ -P ₂	3.11 (1)	C ₁₁ -C ₂₁	1.55 (2)
P ₁ -P ₃	3.55 (1)	C ₃₁ -C ₄₁	1.54 (1)
P ₁ -P ₄	3.48 (1)	O ₁ -O ₂	1.52 (1)
P ₁ -O ₁	3.61 (1)	P ₁ -C ₁₂	1.82 (1)
P ₁ -O ₂	4.25 (1)	P ₁ -C ₁₃	1.83 (1)
P ₂ -P ₄	3.60 (1)	P ₂ -C ₂₂	1.82 (1)
P ₂ -O ₁	3.04 (1)	P ₂ -C ₂₃	1.83 (1)
P ₂ -O ₂	2.99 (1)	P ₃ -C ₃₂	1.82 (1)
P ₃ -P ₄	3.13 (1)	P ₃ -C ₃₃	1.83 (1)
P ₃ -O ₁	3.08 (1)	P ₄ -C ₄₂	1.84 (1)
P ₃ -O ₂	3.17 (1)	P ₄ -C ₄₃	1.83 (1)

Table III. Selected Intramolecular Bond Angles (deg)

Bond	Angle	Bond	Angle
P ₁ -Ir-P ₂	83.5 (1)	C ₃₁ -C ₄₁ -P ₄	113.0 (7)
P ₁ -Ir-P ₃	99.1 (1)	C ₄₁ -P ₄ -Ir	108.1 (3)
P ₁ -Ir-P ₄	97.0 (1)	Ir-P ₁ -C ₁₂	123.2 (3)
P ₂ -Ir-P ₃	175.3 (3)	Ir-P ₁ -C ₁₃	115.5 (3)
P ₂ -Ir-P ₄	99.8 (1)	C ₁₁ -P ₁ -C ₁₂	106.2 (5)
P ₃ -Ir-P ₄	83.8 (1)	C ₁₁ -P ₁ -C ₁₃	101.8 (5)
P ₁ -Ir-O ₁	111.8 (2)	C ₁₂ -P ₁ -C ₁₃	101.5 (5)
P ₂ -Ir-O ₁	86.8 (2)	Ir-P ₂ -C ₂₂	117.7 (3)
P ₃ -Ir-O ₁	88.6 (2)	Ir-P ₂ -C ₂₃	114.1 (3)
P ₄ -Ir-O ₁	151.1 (2)	C ₂₁ -P ₂ -C ₂₂	108.6 (5)
P ₁ -Ir-O ₂	153.1 (2)	C ₂₁ -P ₂ -C ₂₃	104.2 (5)
P ₂ -Ir-O ₂	84.6 (2)	C ₂₂ -P ₂ -C ₂₃	102.9 (5)
P ₃ -Ir-O ₂	91.4 (2)	Ir-P ₃ -C ₃₂	121.9 (3)
P ₄ -Ir-O ₂	108.8 (2)	Ir-P ₃ -C ₃₃	114.2 (4)
O ₁ -Ir-O ₂	43.4 (3)	C ₃₁ -P ₃ -C ₃₂	106.1 (5)
Ir-O ₁ -O ₂	68.6 (4)	C ₃₁ -P ₃ -C ₃₃	105.9 (5)
Ir-O ₂ -O ₁	67.9 (4)	C ₃₂ -P ₃ -C ₃₃	100.3 (5)
Ir-P ₁ -C ₁₁	106.5 (3)	Ir-P ₁ -C ₄₂	114.9 (3)
P ₁ -C ₁₁ -C ₂₁	108.1 (7)	Ir-P ₁ -C ₄₃	122.7 (3)
C ₁₁ -C ₂₁ -P ₂	109.8 (7)	C ₄₁ -P ₄ -C ₄₂	97.9 (4)
C ₂₁ -P ₂ -Ir	108.4 (3)	C ₄₁ -P ₄ -C ₄₃	105.5 (5)
Ir-P ₃₁ -C ₃₁	107.1 (3)	C ₄₂ -P ₄ -C ₄₃	104.5 (4)
P ₃ -C ₃₁ -C ₄₁	107.2 (7)		

Figure 1. An overall perspective view of the $[\text{IrO}_2(\text{DPE})_2]^+$ cation, with the numbering scheme used.

atom coordinates. This required that the structure in fact be redetermined three more times: (i) from a crystal (No. 2) ground spherical, 0.4 mm diameter; (ii) from a prismatic crystal (No. 3) (0.26 × 0.29 × 0.32 mm) that had been heated at 130 (±10)°C for 1 hr; (iii) from the same crystal (No. 3) (after completion of the data collection) heated at 130 (±10)°C for a further 5.5 hr. No outward changes in crystal No. 3 were observed after the first

Table IV. Least-Squares Parameters for the Two Sets of Fluorine Atoms and Certain Cationic Atoms

Atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	Weight
Ir	0.3096 (1)	0.2272 (1)	0.0922 (1)	0.0349 (2)	0.0339 (2)	0.0321 (2)	-0.0014 (2)	0.0032 (2)	-0.0007 (2)	1
P ₁	0.3277 (1)	0.3058 (1)	-0.0173 (1)	0.0445 (15)	0.0298 (14)	0.0382 (15)	0.0005 (12)	0.0031 (12)	0.0037 (12)	1
P ₂	0.1847 (1)	0.2042 (2)	0.0258 (1)	0.0343 (14)	0.0407 (16)	0.0427 (15)	0.0005 (12)	0.0002 (12)	-0.0028 (12)	1
P ₃	0.4287 (1)	0.2538 (2)	0.1671 (1)	0.0382 (15)	0.0406 (16)	0.0374 (15)	-0.0056 (12)	0.0020 (12)	-0.0014 (12)	1
P ₄	0.3750 (1)	0.1116 (1)	0.0522 (1)	0.0337 (14)	0.0370 (15)	0.0349 (14)	-0.0018 (12)	0.0035 (11)	0.0033 (12)	1
O ₁	0.2533 (4)	0.2903 (4)	0.2533 (4)	0.0523 (42)	0.0639 (51)	0.0481 (41)	0.0133 (36)	0.0222 (33)	-0.0208 (36)	1
O ₂	0.2559 (4)	0.1994 (4)	0.1928 (4)	0.0528 (44)	0.0687 (53)	0.0517 (43)	-0.0011 (37)	0.0162 (34)	-0.0122 (37)	1
C ₁₁	0.2650 (6)	0.2623 (6)	-0.0999 (5)	0.0498 (68)	0.0545 (71)	0.0410 (63)	-0.0169 (56)	-0.0046 (52)	0.0054 (54)	1
C ₂₁	0.1806 (6)	0.2542 (7)	-0.0731 (6)	0.0517 (72)	0.0684 (81)	0.0474 (68)	-0.0039 (61)	-0.0068 (55)	0.0153 (60)	1
C ₃₁	0.5064 (5)	0.2037 (6)	0.1160 (6)	0.0345 (58)	0.0422 (64)	0.0643 (71)	-0.0053 (50)	0.0099 (51)	-0.0027 (54)	1
C ₄₁	0.4792 (5)	0.1168 (6)	0.0964 (6)	0.0278 (56)	0.0425 (65)	0.0649 (71)	-0.0003 (48)	0.0099 (51)	-0.0069 (54)	1
P ₅	-0.2533 (2)	0.2137 (2)	0.1556 (2)	0.0541 (19)	0.0574 (21)	0.0583 (20)	-0.0031 (18)	0.0046 (18)	-0.0043 (18)	1
F ₁	-0.1954 (17)	0.2247 (19)	0.0864 (18)	0.0809 (133)	0.1952 (280)	0.1011 (113)	0.0223 (157)	0.0406 (97)	-0.0042 (145)	0.7
F ₂	-0.3120 (13)	0.2776 (10)	0.1139 (14)	0.0807 (107)	0.1775 (84)	0.1433 (249)	0.0193 (68)	0.0166 (123)	0.0464 (95)	0.7
F ₃	-0.3051 (11)	0.1484 (8)	0.1098 (9)	0.1310 (124)	0.0646 (84)	0.1002 (110)	-0.0108 (85)	-0.0187 (98)	-0.0268 (72)	0.7
F ₄	-0.2005 (12)	0.1489 (15)	0.1950 (17)	0.0880 (95)	0.1128 (137)	0.2381 (287)	0.0146 (108)	-0.0467 (135)	0.0550 (150)	0.7
F ₅	-0.2042 (9)	0.2800 (11)	0.2208 (10)	0.0880 (95)	0.1128 (137)	0.1331 (137)	-0.0489 (105)	-0.0467 (135)	0.0550 (150)	0.7
F ₆	-0.3061 (14)	0.2800 (11)	0.2208 (10)	0.0683 (129)	0.2859 (298)	0.0530 (84)	-0.0651 (126)	0.0120 (101)	-0.0571 (111)	0.7
F ₁₁	-0.3162 (40)	0.2466 (66)	0.0952 (33)	0.0720 (378)	0.6502 (157)	0.0393 (187)	0.0512 (695)	-0.0099 (190)	0.0274 (529)	0.3
F ₁₂	-0.2406 (34)	0.1325 (21)	0.1115 (25)	0.1828 (384)	0.1185 (278)	0.1406 (315)	0.0242 (301)	0.0709 (334)	-0.0657 (229)	0.3
F ₁₃	-0.2032 (44)	0.2533 (40)	0.1022 (37)	0.1328 (331)	0.1406 (451)	0.1447 (549)	0.0840 (322)	0.0918 (342)	0.1128 (468)	0.3
F ₁₄	-0.2562 (37)	0.2968 (22)	0.2071 (24)	0.2596 (504)	0.0721 (231)	0.1084 (276)	0.0454 (342)	0.0826 (366)	0.0063 (176)	0.3
F ₁₅	-0.1810 (22)	0.1847 (36)	0.2152 (21)	0.0398 (184)	0.2010 (671)	0.0537 (159)	0.0167 (256)	0.0099 (141)	0.0440 (235)	0.3
F ₁₆	-0.3191 (32)	0.1883 (34)	0.2090 (36)	0.0456 (223)	0.1863 (447)	0.1797 (657)	-0.0185 (257)	-0.0206 (269)	0.1415 (483)	0.3

Table V. Variation in β with Period of Irradiation (crystal No. 4)

Time, hr	0	4	7	13	20	26.5	37	43	51.5	62.5
β°	95.18	95.22	95.35	95.33	95.45	95.52	95.57	95.60	95.72	95.83

Table VI. Variation in β with Period of Heating at 130 (± 10) $^\circ$ C (crystal No. 5)

Time, hr	0	1.0	4.0	15.63
β°	95.65	95.97	96.43	97.27

hour of heating. After another 5.5 hr, the crystal became slightly darker in color and more opaque. After the second data collection, crystal No. 3 was heated again for 6.25 hr at 130 (± 10) $^\circ$ C, during which time it turned dark red and became unsuitable for further data collection.

The three sets of data were refined as described for that from the original prismatic crystal (No. 1), and the results showed that the crystal decomposition that was occurring produced systematic changes in the reflection intensities and hence in the derived atomic parameters. Because the results of this study are of great importance to crystallographers, the details will be submitted for publication in *Acta Crystallographica*. However, the immediate consequences are of relevance to chemists and for this reason some representative results are tabulated below in Table VII. There is a dramatic decrease in the number of observed intensities accompanying a loss of crystallinity and disappearance of the high angle reflections as the crystals are irradiated or heated. It is evident that the decomposition causes an apparent increase in the O-O bond length with an accompanying increase in difference between the lengths of Ir-P₁ and Ir-P₄. In the light of the above results, and in keeping with the observations of Hamilton, Abrahams, and others,¹² it would be more realistic to *double* the estimated standard deviations (quoted in Tables I, II, III and IV) which were obtained from the relatively undamaged crystal (No. 1).

Sets of all intensity data have been deposited with ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc. A listing of structure factor amplitudes is available; see paragraph at end of paper regarding supplementary material.

Discussion of Results

The Prismatic Crystal (No. 1). The overall molecular geometry is as previously reported,³ however, two differences are of prime importance; the two equatorial Ir-P bonds (2.31 and 2.34 Å) are closer in length, and the O-O length is 1.52 Å.

By far the best indication¹³ of the accuracy of a crystal

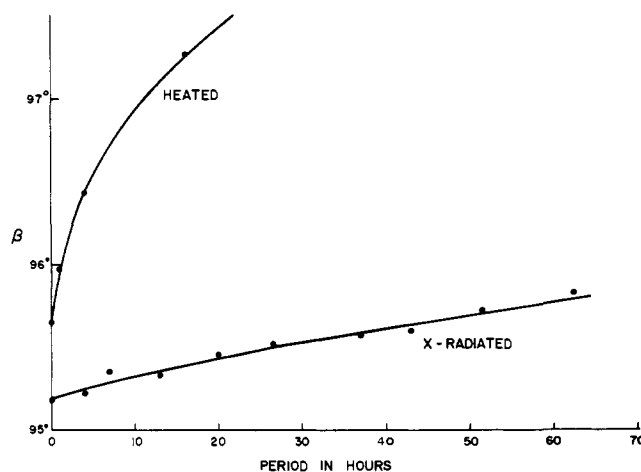


Figure 2. Variation in β with period of irradiation and heating (at 130 (± 10) $^\circ$ C) of crystals No. 4 and 5.

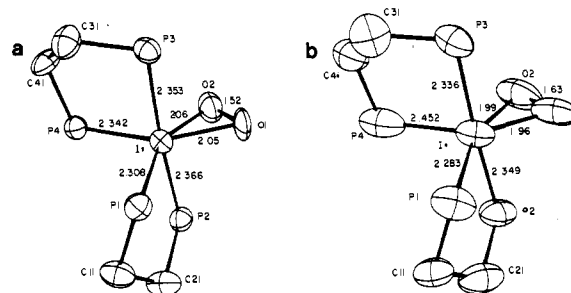


Figure 3. A comparison of the inner coordination in the present (a) and original^{2a} (b) structure determinations.

structure analysis is that chemically equivalent bonds should be equal in length. Observed deviations are a measure of the real accuracy of the determination. It is evident that the two equatorial Ir-P bonds in $[\text{IrO}_2(\text{DPE})_2]^+$ are chemically equivalent and should have similar bond lengths.

Table VII. Comparison of Some Pertinent Structure Parameters of Crystals in Various Stages of Decomposition

	Prismatic (original) (No. 1)	Spherical (No. 2)	Heated 1 hr (No. 3)	Heated 6.5 hr (No. 3)	McGinnety et al.
a , Å	17.18	17.22	17.21	17.23	17.24
b , Å	16.46	16.45	16.45	16.45	16.35
c , Å	16.97	16.94	17.01	17.01	16.98
β , deg	95.02	95.68	96.02	96.16	96.64
Obsd reflections	4007	3743	2814	2749	2177
R	0.044	0.051	0.050	0.061	0.067
O-O, Å	1.52	1.57	1.64	1.74	1.63
Ir-P ₄ , Å	2.342	2.377	2.396	2.433	2.452
Ir-P ₁ , Å	2.308	2.295	2.299	2.295	2.283
Ir x	0.3096	0.3090	0.3087	0.3079	0.3073
y	0.2272	0.2290	0.2299	0.2314	0.2328
z	0.0922	0.0943	0.0951	0.0965	0.0973
P ₄ x	0.3750	0.3749	0.3746	0.3746	0.3729
y	0.1115	0.1119	0.1120	0.1119	0.1114
z	0.0522	0.0525	0.0526	0.0530	0.0522
P ₁ x	0.3277	0.3263	0.3252	0.3237	0.3231
y	0.3059	0.3074	0.3084	0.3101	0.3116
z	-0.0173	-0.0147	-0.0137	-0.0120	-0.0107
P ₄ U_{22}	0.03724	0.05596	0.06867	0.08759	0.1192

This is more nearly so in the present work than in the original.

It is important to note that only 3110 reflections were recorded in the earlier determination with an experimental arrangement similar to that which yielded 4452 reflections in the present study. In addition, the authors state³ that there was a decrease in intensity for the standard reflections, implying decomposition of the sample (which the present study has confirmed). Independent of this, the following is relevant to the differences between the Ir-P lengths observed in the two determinations.

The Ir-P₄ bond length of 2.452 Å in ref 3 is remarkably long and it seems reasonable that this is caused by the parameters associated with P₄. In their Table III, β_{22} for P₄ is 0.0088, which is almost twice the value of β_{22} for any of the Ir, P₁, P₂, P₃, or C₄ atoms. In the Ir-P₄-C₄ bond arrangement, it is unreasonable that P₄ has an amplitude of vibration varying significantly from those of Ir or C₄. Examination of Figure 3b of this paper shows that the longest axis of the ellipsoid of vibration of their P₄ is parallel to the Ir-P₄ bond. This is unlikely as the maximum vibration amplitude is expected to be perpendicular to a bond. Thus, the thermal parameters of P₄ appear to be unreliable in the original work and therefore the positional parameters too may be suspect. Similarly, the derived long bond length of 2.452 Å for Ir-P₄ and the large difference of 0.17 Å between the two chemically equivalent Ir-P bonds would appear to be unreal. This leads to the conclusion that the esd's derived from the least-squares analysis (0.007-0.009 Å) for the Ir-P bond lengths are clearly too small. The vibrational ellipsoids of these phosphorus atoms are reasonably isotropic in the present study, as shown in Figure 3a.

Decomposition Studies. Crystal decomposition takes place both on exposure to X-radiation and on heating, with resultant systematic changes (as well as errors) in the intensity data. Comparison between the various sets of results from the decomposed crystals shows that it is the positional coordinates of the iridium and phosphorus atoms that vary most (up to 50 esd!) as the decomposition progresses. The systematic change in the value of β_{22} of P₄ follows the same pattern as do the changes in the positional coordinates. The anomalous Ir-P and O-O bond lengths are caused by these changes. Caution must therefore be exercised in drawing conclusions about the chemical significance of the bond lengths derived from the decomposed crystals.

Conclusion

It is concluded that the O-O bond length in the [Ir-O₂(DPE)₂]⁺ cation is not unusually long and that the precision of the results is such that a decision cannot be made as

to whether the O-O bond length is different from that found either in the rhodium analogue³ or in other related iridium compounds.^{4,6}

It is also important to note that the reported¹ value of 1.30 Å for the O-O bond length in [IrO₂ClCO(PPh₃)₂] may be an artifact caused by the observed disorder in the crystal, because the O-O distance in the closely related compound⁶ [IrO₂ClCO(PPh₂Et)₂] is 1.46 Å. In addition, we conclude that the widely accepted¹⁵ deductions previously drawn³ about the bonding between the dioxygen moiety and the metal atom are not tenable.

This study emphasises that no matter how carefully the data collection and refinement of a crystal structure are done, the validity of the final results and the inferences drawn from them are dependent on the quality and stability of the crystals used in the determination.

Supplementary Material Available. A listing of structure factor amplitudes of crystal No. 1, 2, and 3 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C., 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-6396.

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